Biogeochemical Processes in Forest Riparian Zones

Conceptualizing Function and Heterogeneity in Boreal Catchments

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Cover: A typical riparian zone in a boreal forest (Bispgården, Sweden)
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Abstract

The area of interaction between terrestrial and aquatic environments, i.e. the riparian zone (RZ), has long been recognized as an important landscape feature from both scientific and management perspectives. Surface water quality is to a great extent regulated by substances exported from RZs. Boreal forest RZs are characterized by high organic matter content, which drives important biogeochemical processes. The overall objective of this thesis was to develop the understanding of RZ biogeochemical processes so as to provide a sound scientific basis for protection of surface water quality in boreal forests. The work was based on measurements from stream, riparian, and upslope monitoring sites in the 68 km^2 Krycklan catchment in northern Sweden. Specifically, the study of dissolved organic carbon (DOC), base cations (BC), silicon (Si), and sulfate (SO_4^{2-}) was included.

Opposite SO_4^{2-} and DOC trends were observed in both stream and riparian water, whereas no trends were apparent in the upslope area. This suggests that RZ processes control stream SO_4^{2-} and DOC independently of upslope soils. On the other hand, the upslope signal of BC and Si was maintained through the RZ and subsequently exported to the streams. RZs were found to have a long-term potential to export DOC from both new and old carbon pools. This, in combination with predicted future climate and exhaustion of residual S pools accumulated during the acidification period, is likely to increase DOC concentrations affecting surface water quality and the global carbon cycle. The hydrological connectivity between RZs and streams can be conceptualized as a 'dominant source layer', the narrow depth range with the highest contribution to solute and water fluxes. Local hydromorphology drives spatial heterogeneity in the distribution of RZs and in the intensity of their biogeochemical functions including retention via interaction with organic matter and transformation via redox reactions.

Overall, this thesis provides new insights into the role of the RZ in catchment biogeochemistry and proposes a conceptualization of its function and heterogeneity. These outcomes are an essential prerequisite for ecologically sustainable and economically effective land management that preserves surface water quality.

Keywords: riparian zone, near-stream, heterogeneity, organic matter, biogeochemistry, climate change, environmental change, catchment science, boreal forest, water quality

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Dedication

A mis padres y hermana

The feeling of awed wonder that science can give us is one of the highest experiences of which the human psyche is capable.

Richard Dawkins

Contents

List of Publications

This thesis is based on the work contained in the following papers, referred to by Roman numerals in the text:

I Ledesma, J.L.J., Grabs, T., Futter, M.N., Bishop, K.H., Laudon, H. & Köhler, S.J. (2013). Riparian zone control on base cation concentration in boreal streams. *Biogeosciences,* 10(6), pp. 3849-3868.

II Ledesma, J.L.J., Grabs, T., Bishop, K.H., Schiff, S.L. & Köhler, S.J. (2015). Potential for long-term transfer of dissolved organic carbon from riparian zones to streams in boreal catchments. *Global Change Biology,* 21(8), pp. 2963-79.

III Ledesma, J.L.J., Futter, M.N., Laudon, H., Evans, C.D. & Köhler, S.J. Boreal forest riparian zones regulate stream sulfate and dissolved organic carbon. (*Submitted manuscript*).

IV Ledesma, J.L.J., Futter, M.N., Blackburn, M., Lidman, F., Grabs, T., Sponseller, R.A., Laudon, H., Bishop, K.H., & Köhler, S.J. Towards an improved conceptualization of riparian zone biogeochemical function in boreal forest headwaters. (*Manuscript*).

The contribution of José L. J. Ledesma to the papers included in this thesis was as follows:

I Planned the study together with co-authors. Had the main responsibility for data handling, data analyses, interpretations, writing, and publishing.

II Planned the study together with co-authors. Carried out soil and vegetation surveys. Had the main responsibility for data handling, data analyses, interpretations, writing, and publishing.

III Planned the study together with co-authors. Had the main responsibility for data handling, data analyses, interpretations, writing, and submission.

IV Planned the study together with co-authors. Had the main responsibility for writing.

Abbreviations

a_c	Specific lateral contributing area
ANOVA	Analysis of variance
BC	Base cations
CO_2	Carbon dioxide
DEM	Digital Elevation Model
DIC	Dissolved inorganic carbon
DOC	Dissolved organic carbon
DSL	Dominant source layer
DTW	Depth-to-water index
FTIR	Fourier transformation infrared spectroscopy
GPP	Gross primary production
ICP-AES	Inductively coupled plasma atomic emission spectroscopy
KCS	Krycklan Catchment Study
LiDAR	Light Detection and Ranging
NEP	Net ecosystem production
OC	Organic carbon
OM	Organic matter
PLS	Partial least squares
POC	Particulate organic carbon
RIM	Riparian flow-concentration integration model
ROK	Riparian Observatory in Krycklan
RZ	Riparian zone
SCP	Specific carbon pool
SIDE	Stream Index Division Equations
SO_4^{2-}	Sulfate
SOCC	Soil organic carbon content
TCP	Total carbon pool
TOC	Total organic carbon
TWI	Topographic wetness index

1 Introduction

Water is one of the most important natural resources for humans. It is used for numerous purposes including food, cleaning, hygiene, agriculture, industry, energy, and recreation. It is therefore essential to preserve surface water quality, which is to a great extent determined by substances mobilized from the surrounding soils. The area of interaction between soils and waters, particularly streams and small rivers, is a key landscape feature. This terrestrial-aquatic interface is referred to as the riparian zone (RZ). Biogeochemical processes taking place in this system are of great importance from both scientific and management perspectives. This thesis provides new understanding of the complex processes occurring in the RZ, needed to preserve surface water quality in boreal forests.

1.1 What is the riparian zone?

The term riparian comes from the Latin *ripa*, which means bank (of a stream or river). The first scientific use of this word is attributed to Carl von Linné, who in 1758 named the sand martin, a bird, as *Riparia riparia*, referring to the bank-nesting habit of this species (Johnson & McCormick, 1979). The RZ can be defined in several ways based on biogeochemical, hydrological, ecological or management criteria so it is often ambiguous to delimitate physical RZ boundaries. For example, the RZ can be hydrologically defined as the last few metres of soil through which water flows before entering a gaining stream (Seibert *et al.*, 2009). A broader definition that can be applied to all disciplines is given by Swanson (1981), who defined the RZ as the zone of direct interaction between terrestrial and aquatic environments. Thus, the basis of the RZ notion lies in the inexorable link between the near-stream processes and their influence on contiguous surface waters. A large fraction of the traditional research on RZs has been in the field of ecology (e.g. Naiman & Decamps,

1997) and agriculture (e.g. Lowrance *et al.*, 1985). In this thesis, the focus is on natural and semi-natural systems, particularly boreal forests, and on the fields of catchment hydrology and biogeochemistry.

A catchment (or watershed in American English) is an area of land where all water from precipitation and surface runoff converges to a single point located at the lowest elevation, i.e. the catchment outlet. Boreal forest catchments will be conceptualized here as a three-unit continuum: upslope area, RZ, and surface water (Figure 1). The boreal landscape covers more than ten million square kilometres of the northern circumpolar region and represents almost one third of the world's forests (Apps *et al.*, 1993; Magnani *et al.*, 2007). In these systems, there is a characteristic transition in the soil configuration from mineral soils in upslope areas, commonly podzols, to organic soils, commonly histosols, in wet low-lying near-stream areas (Chesworth, 2008). Thus, RZs are low-lying soils within the catchment that tend to accumulate water and large amounts of organic matter (OM), important in the biogeochemical processing of most chemical elements (Schlesinger, 1997). Hydrology, i.e. the water movement, distribution, and quantity, is the engine of the processes and drives the mobilization of substances from terrestrial to aquatic systems. Hydrological connectivity between terrestrial and aquatic systems and OM are the central players in RZ biogeochemistry, eventually determining stream chemistry and surface water quality.

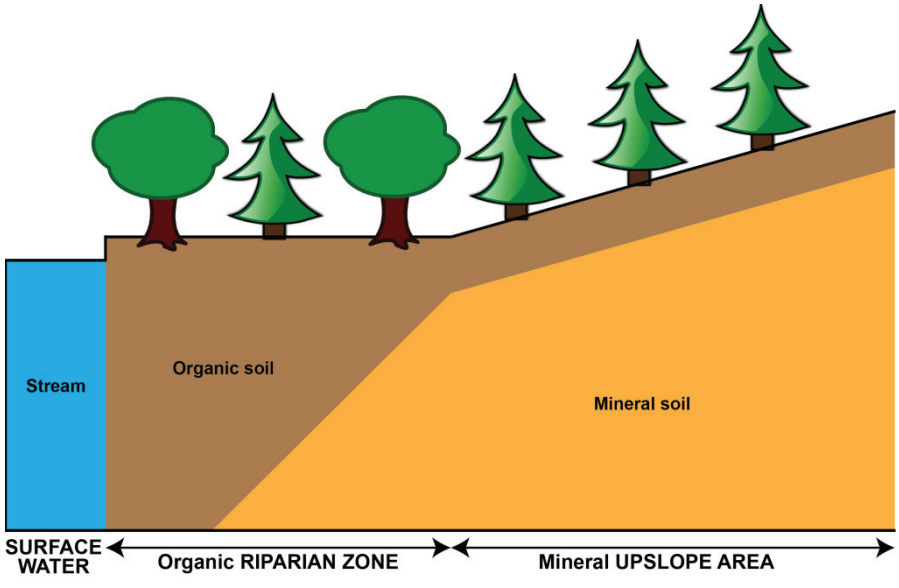

Figure 1. Conceptualization of the boreal forest (soil profile view) as a three-unit continuum including mineral upslope areas, organic riparian zones, and stream.

1.2 Riparian zones and hydrology

Scientists have studied rainfall-runoff processes for over a century. Yet, the questions that hydrologists are currently trying to answer are very similar to those that were asked in the beginning of the 20th century: temporal and spatial hydrograph separation and identification of sources, flowpaths, and residence times of water in catchments (Hewlett *et al.*, 1977, McDonnell *et al.*, 2010). Hewlett & Hibbert (1967) first highlighted the importance of subsurface flow versus traditional Hortonian overland flow in runoff generation. This subsurface flow was mainly formed by 'old' or 'pre-event' water, as indicated by isotopic tracers (Martinec, 1975). Sklash & Farvolden (1979) introduced the groundwater ridging hypothesis as a first attempt to explain the mobilization of 'old' or 'pre-event' water via subsurface flow in stream runoff during hydrological episodes.

Based on those older concepts, the work carried out in Sweden by Lundin (1982), Rodhe (1989), and Bishop *et al.* (1990), among others, gave birth to the transmissivity feedback mechanism concept. This explains how lateral flow movement to the stream increases dramatically as groundwater table rises during precipitation or snowmelt events and water enters the highly conductive layers in the RZ. The result is the large mobilization of 'old' or 'pre-event' water and the convergence of lateral fluxes to a shallow and relatively narrow layer in the riparian soil profile (Schiff *et al.*, 1998). This is a common phenomenon in till soils worldwide (McDonnell *et al.*, 1998; McGlynn & McDonnell, 2003b; Seibert *et al.*, 2003) and dominant in the boreal region (Bishop *et al.*, 2011). The relative contribution of RZs to runoff is thereby disproportionally higher than the contribution of the considerably larger upslope areas (Rodhe, 1989; McGlynn & McDonnell, 2003b). All above mentioned studies highlighted the importance of flowpaths and groundwater responses in the RZ for runoff generation (e.g. Mulder *et al.*, 1990). Gravity as primary force and topography as fundamental factor control flow networks, hydrological connectivity, and water accumulation (Jencso *et al.*, 2009).

1.3 Organic matter, key in boreal forest riparian zones

Boreal forest RZs are characterized by high OM content (Luke *et al.*, 2007). The combination of landscape features and the characteristic climatic and biological factors in boreal RZs favors higher production than decomposition rates and subsequent accumulation of OM. Solute inputs from upslope areas converge in the RZ providing high nutrient availability for primary production (Jansson *et al.*, 2007). The location of RZs in low flat areas involves shallow groundwater tables that result in hypoxia and low decomposition rates (Kögel-

Knabner & Amelung, 2014). Finally, the cool boreal climate limits microbial activity, slowing decomposition processes, and generates low evapotranspiration rates that favour soil moisture and hypoxia.

OM is a complex heterogeneous mixture of compounds derived from plant, animal, and microbial litter biomass (Kögel-Knabner & Amelung, 2014). OM is important for biogeochemical processes because of its large pool of exchange sites that creates a possibility for chemical interchange between the soil particles and the solution. The exchange sites are made up by hydroxyl (-OH) and carboxyl (-COOH) groups which interchange their protons with ions in the solution in a pH-dependent process (Skyllberg *et al.*, 2001). This chemical exchange capacity in combination with the potential to support microbial processes such as redox reactions (Hedin *et al.*, 1998) makes OM able to interact and affect the biogeochemical cycling of most chemical elements (Schlesinger, 1997; Vestin *et al.*, 2008; Herndon *et al.*, 2015). The largest fraction of OM consists of organic carbon (OC) (Mattsson *et al.*, 2009).

A direct consequence of the high OM content is the potential for RZs to export OC to streams (Dosskey & Bertsch, 1994). Both total organic carbon (TOC) and dissolved organic carbon (DOC) are commonly used terms to describe OC dynamics in catchment studies. DOC is operationally defined as the fraction of OC in a water sample that passes through a 0.45 µm pore-size filter, while the retained fraction is particulate organic carbon (POC). The sum of DOC and POC makes up TOC. In many boreal forest streams, the POC fraction is negligible and TOC concentrations become effectively DOC concentrations (Laudon *et al.*, 2004). When exported to the aquatic environment, DOC plays a key role in food web interactions and biodiversity (Williamson *et al.*, 1999; Karlsson *et al.*, 2012), water acidification status (Erlandsson *et al.*, 2011), transport of toxic metals and organic pollutants (Shafer *et al.*, 1997; Dawson *et al.*, 2009), and drinking water production (Lavonen *et al.*, 2015). The lateral export of DOC to streams can also have important implications for the global carbon cycle (Battin *et al.*, 2009).

Hence, RZs are the main source of DOC to streams in boreal and temperate forest catchments, especially during hydrological events (Boyer *et al.*, 1997; Hinton *et al.*, 1998; Köhler *et al.*, 2009; Strohmeier *et al.*, 2013). Stream DOC concentrations increase during (or immediately after) discharge episodes as a consequence of higher groundwater tables and water flowing through upper, more organic-rich layers in the RZ (Laudon *et al.*, 2004). The result is that lateral DOC fluxes from RZs to streams are limited to only a fraction of the total RZ volume. This leads to the question of, if not infinitely as suggested by McGlynn & McDonnell (2003a) and Sanderman *et al.* (2009), how long this

riparian source can possibly sustain the high lateral DOC fluxes in boreal forest catchments. This question was assessed in paper II of this thesis.

1.4 Importance of the riparian zone on headwater stream chemistry

Headwater catchments are quantitatively significant (Benstead & Leigh, 2012) and qualitatively important in the biogeochemistry of larger aquatic networks (Bernal *et al.*, 2012). For example, over 90% of the total stream network in Sweden belongs to catchments with total area under 15 km^2 (Bishop *et al.*, 2008). At this scale, the RZ influence on stream water quality is larger than at downstream locations where riparian signals are attenuated by in-stream processes, mixing of upstream waters, or through increased influence of non-riparian sources (e.g. lake or deep groundwater). Thus, headwaters offer advantages and provide invaluable information when studying biogeochemical cycles (Bormann & Likens, 1967; Peterson *et al.*, 2001). Biogeochemical hot spots are areas that show disproportionately high reaction rates relative to the surrounding matrix, a definition that can be applied to RZs (McClain *et al.*, 2003; Vidon *et al.*, 2010), especially in headwaters. In addition to controlling stream DOC chemistry, RZs are sinks of inorganic nitrogen and sources of organic nitrogen (Cirmo & McDonnell, 1997; Fölster, 2000; Petrone *et al.*, 2007). They retain aluminium (Al) (Pellerin *et al.*, 2002), iron (Fe) (Knorr, 2013), other organophilic metals (Lidman *et al.*, 2014), and organic pollutants (Bergknut *et al.*, 2011), thereby influencing surface water quality.

Base cations (BC), including the essential plant nutrients calcium (Ca), magnesium (Mg), potassium (K), and the less reactive sodium (Na), are important elements in maintaining soil fertility and play an important role in the acidification status of soils and waters. The interplay between plant uptake and litter fall on one hand, and the mechanism of interchange between soil particles and soil solution (mediated by the exchangeable pools of OM and clay particles) on the other hand, control the biogeochemical cycling of BC. The ultimate source of BC is the mechanical, chemical, or biological decomposition of minerals in the process of weathering. Concentrations and fluxes of BC in boreal RZs have not been extensively examined. Such an examination is essential to provide insights into the biogeochemical control by RZs on the lateral transfer of BC to the stream and was investigated in paper I of this thesis. The behaviour of silicon (Si) in forest soils and streams is similar to that of BC as it is also related to weathering and biological growth. Therefore, Si is also a relevant element to study in connection to BC.

The RZ versus upslope regulation of stream sulfate (SO_4^{2-}) is also not well understood and was examined in paper III of this thesis. The speciation of sulfur (S) is controlled by redox reactions, i.e. the transfer of electrons between different chemical species. In the case of SO_4^{2-} formation, the redox reaction is regulated by the availability of oxygen as an electron acceptor. Groundwater tables in forest RZs can be dynamic, leading to a transition between oxic and hypoxic conditions in upper conductive layers (Grabs *et al.*, 2012). This influences riparian and, subsequently, stream SO_4^{2-} concentration and fluxes (Devito & Hill, 1997). SO_4^{2-} is important from a surface water quality perspective because affects acidification status (Futter *et al.*, 2014) and controls DOC solubility (Clark *et al.*, 2006; Evans *et al.*, 2012).

1.5 Riparian zone heterogeneity

The RZ have been traditionally conceptualized as a single unit buffering lotic water bodies. Single representative riparian profiles or single RZ widths are often used to investigate the links between stream and riparian chemistry and hydrology (Boyer *et al.*, 1996; Smart *et al.*, 2001; Sanderman *et al.*, 2009; Seibert *et al.*, 2009; Gundersen *et al.*, 2010; Winterdahl *et al.*, 2011b). This lumped conceptualization omits RZ spatial heterogeneity, leading to potential oversimplifications when upscaling results to catchments and landscapes (Blume & van Meerveld, 2015). Riparian hydrologic responses and solute concentrations and exports are commonly heterogeneous in space along the stream (Vidon & Hill, 2004; Grabs *et al.*, 2012; Zimmer *et al.*, 2013; Herndon *et al.*, 2015). Topography and local hydromorphology drive this heterogeneity as they control preferential flowpaths, water residence times, and connectivity between the catchment and the stream via the RZ (Jencso *et al.*, 2009). Hypothetically, this leads to different rates of OM accumulation and transport both longitudinally along the stream and laterally along the hillslope.

The study of the above described elements and compounds (DOC, BC, Si and SO_4^{2-}) can help in the mechanistic understanding of RZ biogeochemical processes. This understanding is valuable for appropriate RZ conceptualizations, needed for sustainable management of boreal and other surface waters. An integrated conceptualization of hydrological connectivity, RZ biogeochemical functions, and spatial heterogeneity was developed in paper IV of this thesis. This conceptualization was based on integrating biogeochemical and hydrological theory with past and on-going research in boreal forest catchments, including papers I-III.

1.6 Climate and forest management pressures on riparian zone

Biogeochemical processes occurring in the RZ can be affected by external factors, including climate change and forest management (Gauthier *et al.*, 2015). An increase in both temperature and precipitation is forecast for boreal regions (IPCC, 2007), together with changes in precipitation patterns with more extreme events such as droughts (Schlyter *et al.*, 2006). At the same time, changes in energy policy to substitute fossil fuels by renewable sources are increasing the demand of forest biomass obtained by harvesting. Removal of forest biomass decreases BC pools (Belyazid *et al.*, 2006) and lowers evapotranspiration rates (Bosch & Hewlett, 1982).

Both future climate and forestry will have a number of hydrological and biogeochemical implications at the catchment scale. These might include periods of strong dryness and oxidation, rising groundwater tables leading to waterlogged conditions, changes in flowpaths, mobilization of accumulated compounds, increased runoff, and enhance biogeochemical reactions, all of which are likely to have an effect on RZ function and therefore on surface water quality. The broad range of biogeochemical responses to changing climate and implications for forest management were put into context in this thesis.

2 Framework and objectives

The work presented in this thesis was conducted as part of ForWater, a strong research environment project funded by the Swedish Research Council Formas. ForWater aimed to achieve a scientifically based assessment of how pressures from forest management and climate change may affect water quality.

The overall objective of this thesis was to further develop the understanding of RZ biogeochemical processes so as to provide a basis for a continued successful protection of surface water quality. The specific objectives of the thesis were to:

- better understand relationships between BC and Si in RZ soils and adjacent surface waters (paper I),
- quantitatively evaluate the potential of RZs to sustain lateral DOC fluxes (paper II),
- investigate the role of the RZ versus upslope areas in controlling catchment SO_4^{2-} dynamics (paper III),
- conceptualize RZ hydrological connectivity, biogeochemical functions, and spatial heterogeneity (paper IV),
- contribute to the preservation of good water quality in managed boreal forest catchments by linking the new understanding developed here to potential implications for the global carbon cycle, future climate, forest management, and riparian upscaling (papers I-IV).

3 Methodology

The work presented in this thesis was based on long-term data from regular monitoring, targeted sampling, and field surveys from the Krycklan Catchment Study (KCS) site (Figure 2). Long-term environmental monitoring programs are valuable to understand long-term processes in catchment biogeochemistry and for evaluating management strategies (Lovett *et al.*, 2007; Fölster *et al.*, 2014). The study periods were 2008-2009 (papers I-II) and 2003-2012 (paper III). Below, the catchment, the data sources, and the most relevant calculations and analyses are described.

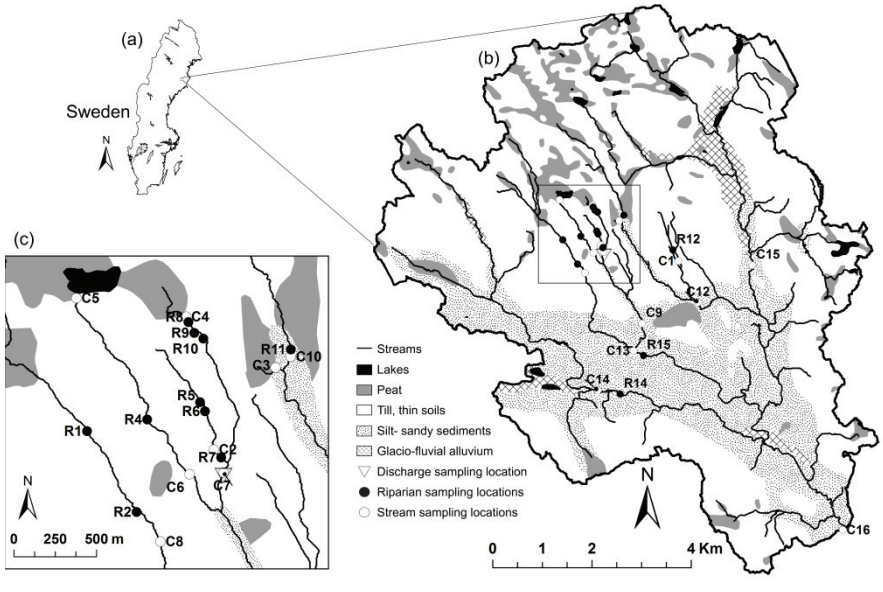

Figure 2. (a): Location of the Krycklan catchment within Sweden. (b): Shape of the Krycklan catchment including sampling site locations and landscape element types. (c) Zoom to the highlighted square in (b). Figure adapted from paper I and paper II.

3.1 Study site: The Krycklan Catchment Study (KCS)

The KCS (Laudon *et al.*, 2013), located in northern Sweden (Figure 2), contains an extensive network of streams, riparian, and upslope monitoring sites that are ideal to investigate terrestrial-aquatic interactions in boreal forest catchments.

3.1.1 Catchment characterization

The KCS includes the upper 68 km^2 of the Krycklan catchment (total area of 121 km^2) and its outlet (64° 12'N 19° 52'E) is located approximately 60 km west from the Baltic Sea and 50 km north-west of the city of Umeå in Sweden (Figure 2). Elevation ranges from 114 to 405 m above sea level, resulting in a gentle topography. The climate is subarctic with a mean temperature of 1.9 ºC and mean annual precipitation of 632 mm $year^{-1}$ (1981-2013), approximately half of it falling as snow. The water balance is divided approximately evenly between runoff and evapotranspiration (Köhler *et al.*, 2008). The 4-6 week period of spring flood contributes between 40% and 60% of the total annual runoff. Land use is dominated by forest (87%) and peat-forming wetlands (9%), characteristic of the boreal ecoregion. Lower proportions of arable lands (3%) and lakes (1%) are sparsely distributed.

The gneissic bedrock consists of Svecofennian rocks with 93% metasediments and metagraywacke, 4% acid and intermediate metavolcanic rocks, and 3% basic metavolcanic rocks (Ågren *et al.*, 2007). This results in a relatively homogeneous mineralogy throughout the catchment dominated by quartz, plagioclase, and K-feldspar (Ledesma *et al.*, 2013). A clear distinction exists between the material overlying bedrock in the upper (44% of the total area) and lower (56% of the total area) parts of the catchment. The material above the highest postglacial coastline (over 250-260 m) consists of Quaternary deposits of glacial till, whereas the material below this altitude consists of unsorted sediments of sand and silt formed by a postglacial river delta varying in thickness up to tens of meters (Figure 2). These two distinct areas within Krycklan will hereafter be named as till and sediment.

Throughout the catchment and especially in the till, well-developed iron podzols are common in dry upslopes. These are mainly covered by stands of scots pine (*Pinus sylvestris*), which make up 63% of the total tree volume in the catchment. Norway spruces (*Picea abies*, 27%) and deciduous stands (10%) of mainly birch (*Betula* spp.) are common in wet low-lying areas including peat-dominated histosol RZs. *Sphagnum* spp. mosses and *Vaccinium* spp. are common in these near-stream organic-rich soils and in wetland areas in the catchment. Immature azonal soils are found in the sediment area below the highest coastline.

Most of the headwater streams were straightened and deepened 50 to 150 years ago. These ditching practices were common to improve drainage and thereby forest productivity in large areas across Fennoscandia. Currently, less than 1% of the total area is harvested per year with no management at all in the 25% of the catchment occupying the central part. The area became a research forest in 1923 and the impact of forest management is low.

3.1.2 Stream network in the KCS (Papers I-III)

The KCS comprises eighteen partially nested subcatchments that have been intensively monitored since 2002 (Laudon *et al.*, 2013). Of these subcatchments, fifteen (Figure 2; Table 1) were used in paper I and three of them (C2, C4, and C7) comprise the Svartberget catchment (0.47 km^2), which has been studied for over 30 years and was included in papers II-III (in paper III only C2 was included).

Table 1. *Stream subcatchment sites within the Krycklan Catchment Study used in this thesis. Corresponding riparian sampling sites within the Riparian Observatory in Krycklan and land use proportions are indicated.*

Site	Name	Stream order	Riparian sites	Area (km^2)	Forest (%)	Wetland (%)	Arable (%)	Lake (%)
C1	Risbäcken	2	R12	0.48	98.0	2.00	0.0	0.0
C2	Västrabäcken	1	R5, R6, R7	0.12	100	0.00	0.0	0.0
C3	Lillmyrbäcken	1		0.04	59.1	40.4	0.4	0.0
C4	Kallkällsmyren	1	R8	0.18	55.9	44.1	0.0	0.0
C5	Stortjänen Outlet	1		0.65	54.0	39.6	0.0	6.4
C6	Stortjärnbäcken	1	R4	1.10	71.4	24.8	0.0	3.8
C7	Kallkällsbäcken	2	R9, R10	0.47	82.0	18.0	0.0	0.0
C8	Fulbäcken	2	R1, R2	2.30	88.1	11.9	0.0	0.0
C9	Nyängesbäcken	3		2.88	84.4	14.1	0.0	1.5
C10	Stormyrbäcken	2	R11	3.36	73.9	26.1	0.0	0.0
C12	Nymyrbäcken	3		5.44	82.6	17.4	0.0	0.0
C13	Långbäcken	3	R15	7.00	88.2	10.3	0.8	0.7
C14	Åhedbäcken	3	R14	14.1	90.2	5.40	3.7	0.7
C15	Övre Krycklan	4		20.1	81.6	14.5	1.5	2.4
C16	Krycklan	4		67.9	87.3	8.70	3.1	0.9

3.1.3 The Riparian Observatory in Krycklan (ROK) (Papers I-II)

The Riparian Observatory in Krycklan (ROK) (Grabs *et al.*, 2012) was established in 2007 to obtain a better understanding of the terrestrial-aquatic interface and the RZ influence on stream water chemistry. It consists of thirteen instrumented riparian soil profiles distributed across the catchment

(Figure 2, Table 2). Locations were selected to cover a representative range of wetness conditions and soil types. These were identified by terrain analysis of 1 m-resolution airborne light detection and ranging (LiDAR) in conjunction with detailed field reconnaissance (Grabs *et al.*, 2012). Ten of the profiles were located in the till area of the catchment, two were in the sediment area, and one was in the transition between till and sediment areas (Table 2). Most of the riparian profiles located in till soils and the transition site had a thick peat layer (>30 cm), whereas the profiles located in the sediment area had very shallow organic horizons over mineral soils, i.e. azonal soils. Each riparian profile was placed 2 to 4 m from the corresponding stream. The instrumentation consists of pairs of ceramic cup suctions lysimeters (nominal filter pore size 1 ± 0.1 µm) at five equally distributed soil depths (15, 30, 45, 60, and 75 cm) and a perforated PVC tube equipped with an automatic waterlogging device (Figure 3). Hence, soil water chemistry and groundwater levels can be monitored. In this thesis, the ROK locations were classified following Grabs *et al.* (2012) according to parent material and median groundwater table in four classes: (1) till-dry, (2) till-humid, (3) till-wet, and (4) sediment (Table 2). Both the stream and RZ sample collection locations will be referred to as sites hereafter.

Table 2. *Characteristics of the thirteen riparian sampling sites within the Riparian Observatory in Krycklan. Median groundwater table during 2008-2009, topographic wetness index (TWI), soil organic carbon content (SOCC), specific carbon pool per square metre of riparian zone (SCP), dissolved organic carbon flux during 2008-2009 (DOC flux), total carbon pool in a 1-m stream bank (TCP), dominant source layer for DOC (DSL), and riparian zone (RZ) width are indicated.*

Site	Class	Median groundwater table (cm)	TWI	Mean SOCC (%)	SCP (kg m^{-2})	DOC flux (g m^{-2} y^{-1})	TCP (kg m^{-1})	DSL thickness (cm)	RZ width (m)
R4	Till-dry	-59	4.2	4	34.6	2.0	93	28.6	3.3
R12	Till-dry	-62	3.6	5	57.1	2.1	78	53.1	2.3
R1	Till-dry	-53	8.0	17	86.6	3.4	694	40.9	12.0
R9	Till-dry	-50	4.7	14	90.9	7.1	157	42.3	3.1
R7	Till-humid	-48	6.0	50	48.5	15.5	1186	56.5	38.8
R10	Till-humid	-27	7.7	52	22.9	6.6	319	26.2	16.3
R6	Till-humid	-17	8.3	38	82.8	17.6	2743	28.8	39.0
R5	Till-humid	-17	5.6	38	82.8	8.7	1213	25.0	17.1
R2	Till-wet	-13	11.1	45	70.7	20.6	2718	21.4	40.4
R8	Till-wet	-8	8.6	52	30.5	14.7	2738	17.8	90.6
R11	Till-wet	-6	9.1	32	108	10.0	1836	12.7	17.0
R15	Sediment	-58	4.9	2	29.2	4.1	292	74.8	10.0
R14	Sediment	-2	9.2	3	57.1	1.2	114	38.0	2.0

3.1.4 The S-transect (Paper III)

The S-transect was installed in 1995 in a hillslope located in Västrabäcken (Table 1), i.e. stream site C2 in Krycklan (Figure 2), to investigate the upslope-riparian-stream continuum (Köhler *et al.*, 2009). The catena consists of three soil profiles located at 4 (S4), 12 (S12), and 22 (S22) meters from the stream following the local topographic slope and thereby the likely hydrological flowpaths. The profiles represent, respectively, riparian peats, transitional soils, and upslope podzols within the catchment. As at the ROK sites, each profile includes ceramic suction lysimeters for soil water chemistry and data loggers for groundwater levels. Six to seven single lysimeters are located at soil depths varying between 10 to 65 cm (S4), 5 to 70 cm (S12), and 6 to 90 cm (S22).

3.2 Sampling, laboratory analyses, computations and field measurements

As part of the regular monitoring program in KCS, stream water samples and soil water samples from the S-transect are collected with a frequency that varies from monthly during low winter flow to two days-weekly during spring flood (Laudon *et al.*, 2013). Soil water samples from the ROK sites were manually collected from the lysimeters on eight field campaigns (June to October in 2008 and June to September in 2009) using acid-washed Milli-Q rinsed Duran glass bottles (Grabs *et al.*, 2012) (Figure 3). All stream and soil water samples were kept dark and cool prior to being subsampled and analyse within 24 h or frozen for posterior chemical analysis. From water samples, OC was measured as TOC (papers II-III) by a Shimadzu TOC-5000 elemental analyser using catalytic combustion. Importantly, stream (Ågren *et al.*, 2007) and soil water (Ledesma *et al.*, 2015) in Krycklan show no statistically significant difference between DOC and TOC concentrations, suggesting that both are effectively equivalent. Therefore, the term DOC is used here. BC, Si (paper I), and S (paper III) were measured using inductively coupled plasma atomic emission spectroscopy (ICP-AES) and SO_4^{2-} (paper III) was measured by liquid ion chromatography. A subset of water samples from 1999 and 2007 from the three streams in Svartberget (C2, C4, and C7) were analysed for $DO^{14}C$ (paper II). Filtered samples were acidified to pH 4.0 and stored in amber glass. Subsequently, samples were evaporated to dryness in a freeze-drier, combusted to carbon dioxide (CO_2), and purified in an offline vacuum glass line. Continuous flow isotope ratio mass spectrometry was used to analyse $\delta^{13}C$. Purified CO_2 was analysed for ^{14}C by tandem accelerator mass spectrometry. All ^{14}C values were corrected using the measured $\delta^{13}C$.

In August 2008, soil pits close to and representative of the existing ROK sites were excavated for soil and mineral characterization of the instrumented profiles installed in 2007. Small spades, peat samplers, and bulk density cylinders were used to collect soil samples, which were stored cool in plastic bags with zip locks to hinder air intrusion. Two to five samples at different depths were analysed for soil organic carbon content (SOCC) (Table 2) by combustion (paper II). Mineralogical identification and semi-quantitative determination of these samples (paper I) was done by X-ray diffraction (PANalytical X'Pert Pro PW3050/60) and Fourier transformation infrared spectroscopy (FTIR, Perkin Elmer spectrum 100). Soil samples were also collected from each depth where a suction lysimeter was installed in the S-transect profiles. These samples were analysed for total S content (paper III) using an ECS 4010 Elemental Combustion System (Costech International S.p.A).

Long-term stream water discharge records exist for stream site C7 in Krycklan (Figure 2). Discharge here was continuously measured using a 90° V-notch weir within a heated hut. Established stage-discharge rating curves were used to calculate daily discharge values from the water levels monitored at the weir (papers I-II). Following previous studies (Ågren *et al.*, 2007; Köhler *et al.*, 2008; Wallin *et al.*, 2010), specific discharge was assumed to be the same in all Krycklan subcatchments and therefore used to calculate fluxes from all stream and ROK sites (papers I-II). Stream water discharge at the outlet of stream site C2 (Figure 2) was also calculated using an establish stage-discharge rating curve with data from a water level logger that records hourly water heights in a 90° V-notch in the stream (paper III). Hourly groundwater tables were measured at the automatic loggers located at the ROK and S-transect profiles and averaged to daily values.

The RZ widths of the ROK sites were determined based on field observations similar to the method by McGlynn & Seibert (2003), using soil type changes from organic/transitional soils to podzols as the main criterion. Specific lateral contributing areas (a_c) (paper II), normalized to 1-m stream bank, represent the combined riparian and upslope areas that contribute to flow to a specific location along the stream. These were estimated for every ROK site using the multiple deterministic infinite-directional triangular facets flow algorithm (Seibert & McGlynn, 2007) in combination with the Stream Index Division Equations (SIDE) algorithm (Grabs *et al.*, 2010) in a hydrologically corrected, 5-m resolution Digital Elevation Model (DEM). The DEM was also used to compute topographic wetness index (TWI) (Beven & Kirkby, 1979) for every ROK site. The TWI is a surrogate for shallow groundwater table positions and it is defined as $\ln (a_c/\tan\beta)$, where β is the local slope.

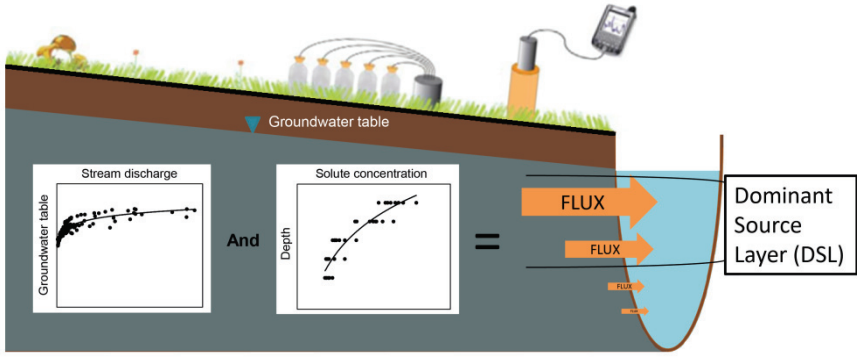

Figure 3. Conceptualization of riparian sampling site instrumentations, the riparian flow-concentration integration model (RIM) approach, and the dominant source later (DSL). Glass bottles are used on the surface to extract lysimeter soil water using vacuum. A data logger within a PVC tube is used to record groundwater levels. RIM integrates lateral discharge profiles (from the stream discharge-groundwater table relationship) and solute concentration profiles to estimate lateral solute fluxes. The DSL is the depth range within the RZ with the highest contribution to solute and water fluxes to the stream.

3.3 The riparian flow-concentration integration model (RIM) (Papers I-III)

The Riparian Flow-Concentration Integration Model (RIM) approach was first explained by Bishop *et al.* (2004) and mathematically described by Seibert *et al.* (2009). The approach is based on the transmissivity feedback mechanism and the integration of lateral flow rates and vertical solute concentration profiles in the RZ. The hydrological assumptions of RIM include: horizontal water flux occurs in the direction of the hydraulic gradient; lateral flow follows Darcy's law and only occurs in saturated layers below the groundwater table; and all water passes the RZ before discharging into the stream (Seibert *et al.*, 2009). Chemically, RIM assumes that the solute concentration signal at every depth in the riparian profile is imprinted instantaneously to the water moving laterally at that specific layer. From those bases and assumptions, RIM can be applied in two distinct ways: (1) as a model at the catchment scale to explain stream chemical variability (Winterdahl *et al.*, 2011a, 2011b; Eklöf *et al.*, 2015); or (2) at the soil profile scale to quantify lateral fluxes from RZs to streams. This second approach is analogous to the way in which riverine fluxes are estimated and it was used in this thesis in papers I-III, whereas no actual modelling of stream chemistry was attempted in any case. Note that RIM was developed to be used in RZs but in principle can be applied to any soil, sediment or weathered parent material (e.g. to estimate lateral fluxes from upslope soils to RZs as in paper III). Previously, RIM have been used to

calculate lateral fluxes of DOC (Köhler *et al.*, 2009; Ågren *et al.*, 2010), dissolved inorganic carbon (DIC) (Öquist *et al.*, 2009), organic and inorganic nitrogen (Petrone *et al.*, 2007); Al (Cory *et al.*, 2007), and lead (Pb) (Klaminder *et al.*, 2006) in a similar manner as in this thesis. The method will be summarized below.

In short, for a given soil profile, RIM is derived from the relationship between daily stream discharge and daily groundwater tables (Figure 3). This relationship is usually best fitted by an exponential curve if groundwater table is the independent variable (papers I-II) or, equivalently, by a logarithmic curve if stream discharge is the independent variable (paper III). Thus, from the equations describing these curves, it is possible to calculate or back-calculate daily groundwater tables for time series with gaps (papers I-III), as stream discharge data are usually more readily available than groundwater table data. Under the hydrological assumptions of RIM, it is possible to derive a lateral discharge profile. At any given time, the amount of water moving laterally through a soil profile following Darcy's law is equivalent to the stream discharge (normalized to surface area). Because of the direct relationship between stream discharge and groundwater table position, it is possible to estimate lateral flows for any given stream discharge at any given soil layer (that are obviously proportional to the stream discharge-groundwater table curve) (Figure 3). The lower limit of the profile can be set to an appropriate depth of hydrologically active soil, e.g. 1 or 2 m. Because the water flux in the deeper soil is several orders of magnitude lower, changes in the assumed hydrological depth will have a negligible influence in the calculations. The next step is to interpolate both in time (for the given period of study) and in space (in the soil vertical profile) the measured chemical concentration in soil water to generate daily chemical profile time series. Once both the lateral discharge profile and the chemical concentration profile are built, it is trivial to integrate them (always below the groundwater table) to estimate fluxes or flow-weighted concentrations for any specific period of time or any specific soil layers. In this thesis, RIM was used to calculate flow-weighted concentrations of BC and Si in the ROK sites (paper I), to calculate fluxes of DOC in the ROK sites (paper II), and to calculate flow-weighted concentrations and fluxes of SO_4^{2-} and DOC in the S-transect profiles (paper III).

3.4 Statistical analyses

A series of analyses of variance (ANOVAs) were performed to estimate the relative contribution of site class (Table 2), time, and depth of sampling to the

total variation in BC and Si concentrations in the ROK sites (paper I). The fraction of total variation ascribed to each component was equal to the sum of squares for that component divided by the total sum of squares from the ANOVA (Futter *et al.*, 2011). In the stream sites, BC and Si flow-weighted concentrations were set as response variables and landscape element-type proportions (open water, peat, bedrock, till, silt, sand, alluvial, gravel, and thin soils) in the corresponding subcatchments were set as predictors in a partial least squares (PLS) analysis (Chin *et al.*, 2003). This was done to explore geologic controls on BC and Si concentrations from catchments with different landscape element-type proportions (paper I).

The variation of estimated annual DOC fluxes from the ROK sites was tested against five independent variables including median groundwater table, TWI, specific carbon pool (SCP), total carbon pool (TCP), and RZ width (Table 2) by a combination of simple and multiple linear regressions (paper II). The total independent contribution and the joint influence of these variables (predictors) were calculated using a hierarchical partitioning analysis (Chevan & Sutherland, 1991; Mac Nally, 2002). This was done in a multiple linear regression model where the estimated DOC flux was the response variable. A randomization test was carried out to determine which of the five variables were statistically significant and thus retained in the model (paper II).

Monthly averages of SO_4^{2-} and DOC concentrations from the stream and all soil water lysimeters in the S-transect were used in a Mann-Kendall test (Mann, 1945; Libiseller & Grimvall, 2002) to evaluate the significance of annual trends (paper III). Other uncertainty and sensitivity analyses are described in detail in papers I-III.

4 Results and Discussion

4.1 The riparian zone can alone support stream DOC fluxes (Paper II)

In paper II lateral DOC fluxes were compared to the total carbon pool in the thirteen ROK riparian profiles (Table 2). Hence, theoretical turnover times were investigated. All OC was assumed to originate in the RZ with a negligible contribution from the upslope area. This approach was appropriate to test whether the RZ alone can sustain DOC exports. Dissimilarities between upslope C quality and riparian and stream C quality in the KCS (Maehder, 2012; Kothawala *et al.*, 2015) and other sites (Sanderman *et al.*, 2009) support a negligible influence of upslope areas in the transfer of DOC to streams.

The theoretical turnover times were on the order of hundreds to a few thousands of years, representing how long it would take to empty the riparian carbon pools at the current constant rate of leaching derived from the estimated exports. Thus, there is a potentially long-lasting supply of DOC from RZs to streams in boreal forest catchments. Importantly, the theoretical turnover times were estimated for the 'dominant source layer' (DSL). The DSL concept, as introduced in this thesis, can be broadly defined as the narrow depth range within the RZ having the highest contribution to solute and water fluxes to the stream (Figure 3). This concept is based on the exponential decrease in hydraulic conductivity with depth in the RZ, which implies that lateral flowpaths converge to a relatively narrow layer (i.e. the DSL), as suggested by Schiff et al. (1998). In paper II, the DSL was arbitrarily defined as the depth range within the RZ with the highest contribution per unit depth to 90% of the mean annual DOC flux. The DSL thickness at the thirteen ROK sites varied from 13 to 75 cm with a mean value of 35.9 ± 17.6 (±SD) cm (Table 2). Therefore, a layer of approximately 40 cm within the riparian soil profile was responsible for 90% of the DOC lateral flux to the stream during 2008-2009.

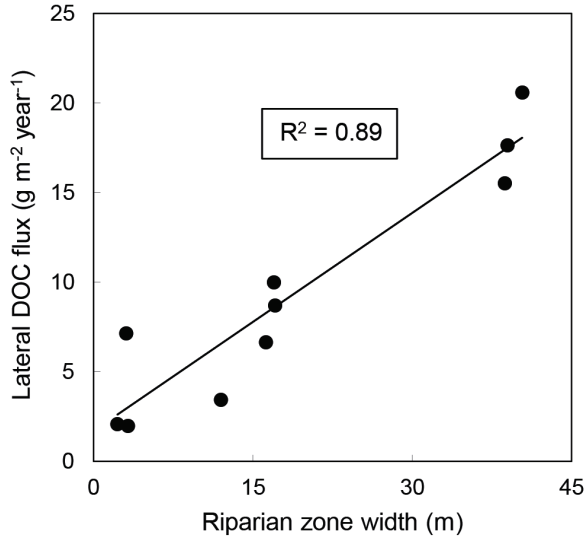

Figure 4. Simple linear regression model to predict lateral dissolved organic carbon (DOC) fluxes in boreal forest riparian zones on till from riparian zone widths. Ten of the thirteen Riparian Observatory in sites in Krycklan are displayed (sites on forest till). Figure adapted from paper II.

The magnitude of the lateral DOC fluxes (8.7 ± 6.5 g C m^{-2} $year^{-1}$) (Table 2) was controlled by local hydromorphological characteristics. Specifically, the RZ width explained roughly 90% of the variation in DOC fluxes for the ROK sites on forest till (Figure 4). Median groundwater table and TWI (Table 2) also explained about 50% of the variation each. The hierarchical partitioning analysis that was carried out showed a high joint influence between these explanatory variables of riparian DOC fluxes. RZ width had the highest independent effect. This was interpreted as an interconnection of different processes: a greater RZ width (based on the lateral extent of histosols) is an indication of persistent wet/hypoxic conditions that limit degradation and favor build up organic soils with shallow groundwater tables and high TWI that lead to high potential lateral DOC fluxes (Figure 5).

The majority of the OC found in the aquatic system was of recent origin (i.e. fixed from the atmosphere after 1950), as indicated by the use of isotopic $DO^{14}C$ measurements in stream water samples (sites C2, C4, and C7 in Table 1). A rough estimate of net ecosystem production (NEP) was used to explore whether the annual net production of new carbon in the RZ was enough to maintain the lateral DOC fluxes. The NEP is defined as the imbalance between gross primary production (GPP) and total respiration (Chapin *et al.*, 2006; de Wit *et al.*, 2016) and corresponds to the carbon fixed from the atmosphere that is available for soil storage or lateral export (Figure 5). Using the NEP from a

neighbouring catchment with similar characteristics to the near-stream low-lying areas in the KCS (NEP = 120 g C m^{-2} $year^{-1}$; Öquist & Laudon, 2008) and accounting only for the riparian area, it was demonstrated that primary production in the RZ could be enough to maintain catchment DOC exports. The NEP could also be enough to support the lateral DIC flux, based on an estimated flux of 3.2 g C m^{-2} $year^{-1}$ from riparian site S4 of the S-transect (as estimated by Öquist *et al.*, 2009), similar to riparian site R5 of the ROK. Thus, despite the large store of carbon in the RZ equivalent to hundreds to a few thousands of years of fluxes at present rates, the dynamic allocation of new carbon from riparian production, rather than the solubilisation and mobilization of old carbon from the riparian pool, seems to control DOC outputs (Figure 5).

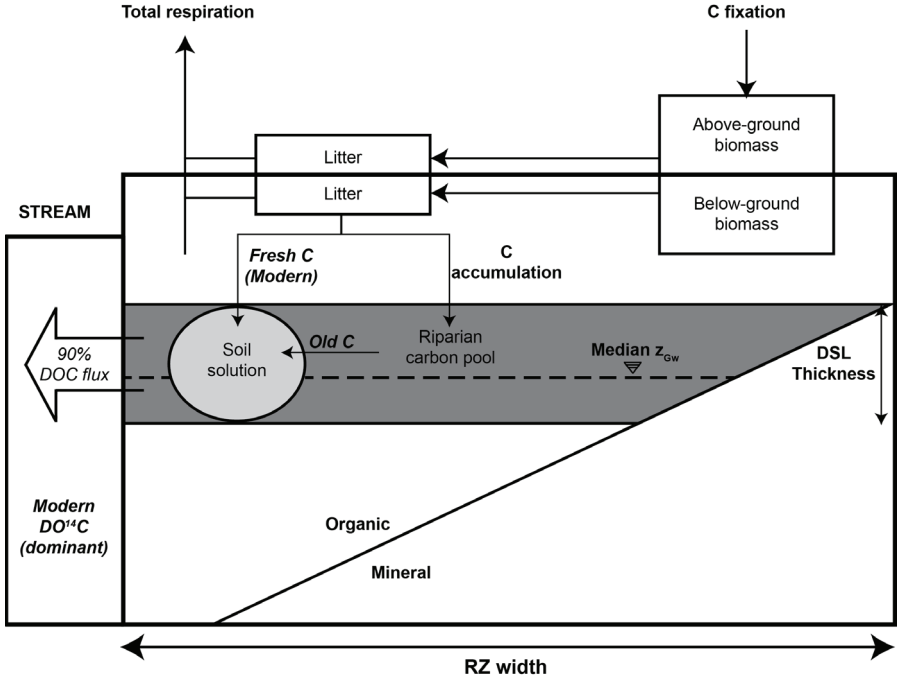

Figure 5. Conceptual diagram of dissolved organic carbon (DOC) mobilization from riparian zones (RZs). Higher lateral DOC fluxes will be found in RZs with more superficial dominant source layers (DSL), which would imply shallower groundwater levels (z_{Gw}), greater RZ widths, and larger riparian carbon pools. The annual input of carbon available for export (DOC flux) or storage (C accumulation) is given by the difference between the carbon fixed from the atmosphere and the total respiration. DOC in the soil solution will be made up by a fraction of modern carbon from production (mainly microbial degradation of below-ground biomass litter) and a fraction of old carbon solubilized from the riparian carbon pool. Stream $DO^{14}C$ measurements suggested that the input of modern carbon from primary production is quantitatively more important than the mining of old carbon from the riparian carbon store. Figure adapted from paper II.

4.2 Riparian zone control on base cations and sulfate (Papers I and III)

Concentrations and flow-weighted concentrations of BC and Si from the ROK and stream sites of Krycklan were investigated in paper I. The main conclusion from this study was that there is a distinct upslope mineralogical signal imprinted in the solution chemistry that is maintained through the RZ and subsequently exported to the stream. Several observations and analyses supported this inference. First, BC and Si concentrations showed a general temporal stability in riparian soil solution, similar to reported upslope subsurface flow signals from a North American catchment (Burns *et al.*, 1998). An ANOVA analysis showed a negligible influence (≤1.0%) of the time of sampling in the variation of BC and Si concentrations. Furthermore, Mg/Ca ratios were notably stable in space and time in both riparian and stream waters (Figure 6). Changes in Mg/Ca ratios over time and among different riparian site classes or stream sites could indicate ion-exchange reactions in the RZ. The stable Mg/Ca ratios suggest that ion exchange could be relatively unimportant in the transfer of divalent BC from RZ to streams. Instead, it was suggested that the stable Mg/Ca ratios were connected to the remarkably homogenous mineralogy within riparian sites. Minerals found in riparian soil samples were quartz (31-43%), plagioclase (20-25%), K-feldspar (16-33%), amphibolites (7-21%), muscovite (2-16%), and chlorite (1-4%). The mineral content proportions were similar for all thirteen ROK sites except for riparian site R9 (excluded from the aforementioned ranges). Interestingly, riparian site R9 deviated from the general stability in Mg/Ca ratios, with higher and more variable values (Mg/Ca = 0.63 ± 0.34) than the other riparian sites (Mg/Ca = 0.35 ± 0.10) (Figure 6). The higher content of Mg-rich chlorite (5-21%) found in riparian site R9 would explain the relatively higher Mg concentrations. The stable mineralogy within the Krycklan catchment was also supported by stable uranium and lanthanum patterns (Köhler *et al.*, 2014). In addition, the PLS analysis of geologic controls on BC and Si flow-weighted concentrations in the stream sites showed a statistically significant contribution of the proportion of Quaternary deposits to the overall signal. The most important predictors in the PLS model were percentage of peat (negatively correlated), and percentage of silt (positively correlated). This further supported our conclusion and the importance of weathering and mineralogy in the export of BC in boreal catchments.

When comparing flow-weighted concentrations from RZs and headwater streams, a good correspondence for Ca, Mg, and Na was found. The RZ could to some limited extent be exchanging these elements maintaining a continuous net release and relatively constant soil solution concentrations. This suggests

RZ may be a passive conduit for these elements. In the case of Si, riparian flow-weighted concentrations were notably higher than stream flow-weighted concentrations. This was interpreted as a retention of this element via accumulation by plants within the RZ, as previously suggested (Struyf & Conley, 2009; Struyf *et al.*, 2009). The poor correspondence between stream and riparian K flow-weighted concentrations and the larger variability of this element´s concentration could be explained by a larger influence of vegetation on internal K cycling (Tukey, 1970).

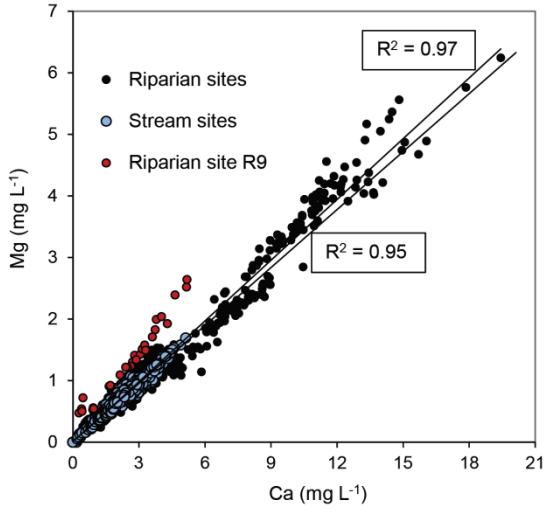

Figure 6. Relationship between magnesium (Mg) and calcium (Ca) in stream water samples and riparian soil water samples from the Krycklan catchment (2008-2009). Coefficient of determinations (R^2) of the linear regression are indicated for riparian samples (except site R9 samples, above) and for stream samples (below). Figure adapted from paper I.

In paper III, one riparian soil profile was used in combination with data from an intermediate and an upslope soil profile (the S-transect) to investigate the role of the RZ versus upslope in controlling catchment SO_4^{2-}. Significant negative trends over time in SO_4^{2-} concentrations were observed for stream water and most soil layers (including the DSL depths) in the RZ and transitional soil, whereas no significant SO_4^{2-} trends were found in the upslope profile (Table 3). The magnitude of the annual decrease in SO_4^{2-} over time was higher in the RZ (>0.2 mg S L^{-1} $year^{-1}$ or >80% decrease) than in the transitional soil (around 0.08 mg S L^{-1} $year^{-1}$ or about 40% decrease), and intermediate in the stream (0.13 mg S L^{-1} $year^{-1}$ or 65% decrease). Comparisons between annual flow-weighted concentrations and fluxes in the three soil profiles and in the stream revealed strong correlations between the stream and the riparian site, which became weaker in the transitional site, and

non- significant in the upslope site. Altogether, the correspondence in stream and riparian negative trends over time, the good correlation between flow-weighted concentration and flux dynamics in the stream and the RZ, and the lack of trend and correlation with the upslope soil demonstrated that the RZ, in contrast to the upslope areas, controls annual and long-term stream SO_4^{2-} dynamics.

Table 3. *Sulfate (SO_4^{2-}) and dissolved organic carbon (DOC) concentration trends (2003-2012) in stream (C2), riparian (S4), transitional (S12), and upslope (S22) waters, including theilslope and significance level from Mann-Kendall analyses. The coefficient of determination (R^2) of the relationship (as a power function) between DOC (dependent variable) and SO_4^{2-} (independent variable) for the stream water and soil water at every lysimeter is also indicated. The percentage of time that a lysimeter depth was below the groundwater table is indicated in column 3.*

Location	Depth (cm)	Saturation percentile (%)	SO_4^{2-} Theil's slope (mg L^{-1} yr^{-1})	DOC Theil's slope (mg L^{-1} yr^{-1})	DOC-S-SO_4^{2-} R^2
C2	-	-	-0.13**	0.70**	0.40***
S4	10	0.0	N.S.	N.S.	N.S.
S4	25	2.3	-0.28**	-3.96**	N.S.
S4	35	23	-0.27**	2.78**	0.73***
S4	45	72	-0.22***	2.22**	0.77***
S4	55	99	-0.22**	1.96**	0.74***
S4	65	100	-0.23**	2.21**	0.80***
S12	5	0.0	N.S.	N.S.	0.37**
S12	10	0.0	N.S.	N.S.	0.23*
S12	20	0.0	N.S.	N.S.	0.45*
S12	30	1.7	-0.08**	0.38*	0.37***
S12	40	13	-0.08**	0.30*	0.31***
S12	60	84	-0.07**	0.31*	0.34***
S12	70	99	-0.08**	0.25**	0.44***
S22	6	0.0	N.S.	N.S.	N.S.
S22	12	0.0	N.S.	N.S.	0.66***
S22	20	0.0	N.S.	N.S.	0.19*
S22	35	0.4	N.S.	N.S.	N.S
S22	50	5.6	N.S.	N.S.	N.S
S22	75	46	N.S.	N.S.	0.78***
S22	90	80	N.S.	0.20***	N.S

- not applicable
N.S. non-significant
* $p<0.05$
** $p<0.01$
*** $p<0.001$

The mechanism of SO_4^{2-} mobilization in the RZ is likely the mineralization of S-bearing organic material by specialized bacteria during oxic conditions (Strickland & Fitzgerald, 1987; Houle *et al.*, 2001). In Krycklan, this is supported by a stream isotope signature (Björkvald *et al.*, 2009), similar to other boreal catchments (Mörth *et al.*, 2005). Transformations of S are therefore driven by moisture status and transient redox conditions (Devito & Hill, 1997; Eimers *et al.*, 2003; Clark *et al.*, 2005). This finding is also supported by our analyses: antecedent annual average groundwater table in the RZ explained most of the variation in riparian SO_4^{2-} concentrations. Groundwater table drawdowns were thus responsible for episodic increases in SO_4^{2-} in both the riparian solution and the stream, which is presumably causing a decline in residual S pool accumulated during the acidification period. On the contrary, the mechanism of SO_4^{2-} mobilization in the upslope is likely a slow desorption of previously adsorbed SO_4^{2-} on mineral surfaces (Houle *et al.*, 2001; Borken *et al.*, 2011; Löfgren *et al.*, 2011), which can last for several decades (Manderscheid *et al.*, 2000; Alewell, 2001). This was supported by the magnitude of the estimated SO_4^{2-} flux from the upslope site S22 (about 4 kg S ha^{-1}), which was comparable to the high atmospheric inputs of SO_4^{2-} during the acidification period in Europe.

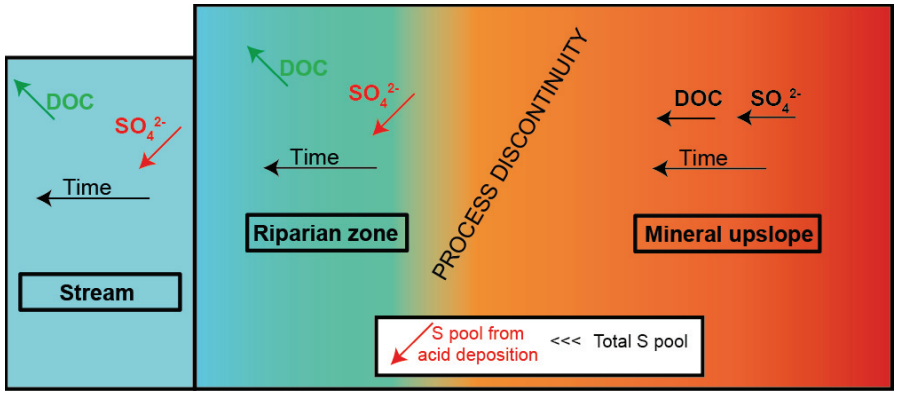

Figure 7. Conceptualization of the disconnection between upslope and riparian zone (RZ) in controlling stream sulfate (SO_4^{2-}) and dissolved organic carbon (DOC). SO_4^{2-} is decreasing and DOC is increasing over time in both RZ and stream, whereas no changes are observed in the upslope. The residual sulfur (S) pool from the acidification period is presumably decreasing, however this is a small fraction of the total S pool in the catchment.

As previously mentioned, OC production in the RZ can sustain lateral DOC fluxes and upslope areas seem to be disconnected with respect to exported carbon in boreal catchments. The short- and long-term covariation between SO_4^{2-} and DOC in the stream and soil transect were remarkably consistent. In

the long-term, positive trends in DOC concentrations and negative trends in SO_4^{2-} concentrations were observed in the stream and the DSL in the RZ, whereas no trends were observed in the upslope mineral soil (Table 3). In the short-term, power functions of DOC versus SO_4^{2-} concentrations explained >70% of the variability in DOC in the soil water samples from all riparian layers hydrologically connected to the stream (Table 3). In stream samples, the explained variation was 40%. In soil water samples from the upslope mineral podzol, there was no significant relationships between SO_4^{2-} and DOC concentrations in most layers. All of these findings are further evidence of the chemical disconnection between stream and upslope areas for SO_4^{2-} and DOC, demonstrating that processes occurring in the RZ control stream chemistry (Figure 7). Moreover, this indicates that SO_4^{2-} is still an important driver of DOC trends in northern headwater catchments, and likely, in other boreal and temperate catchments affected by acidification.

4.3 Proposed conceptualization of riparian zone hydrological connectivity, biogeochemical function, and heterogeneity (Paper IV)

For a practical RZ conceptualization, it is necessary to first define the RZ in terms of its morphology. In paper IV, the RZ was defined as the area between the edge of the stream and the characteristic transition between organic histosols and mineral soils in boreal forest catchments. The proposed conceptualization was focused on boreal headwaters (from a few hectares to a few square kilometers), where riparian organic soils hydrologically connected to stream are commonly underlain by till (Chesworth, 2008). Hydrology and OM accumulation in the RZ are the two key factors determining surface water quality and were the basis of the conceptualization of RZ hydrological connectivity, biogeochemical function, and heterogeneity.

Following previous suggestions for river systems (Ward, 1989), a four-dimensional pattern of hydrological connectivity in catchments was proposed. This included (1) laterally along the hillslope, (2) longitudinally along the stream, (3) vertically down the riparian profile and (4) temporally through event-based and seasonal changes in hydrology (Figure 8a). Mapping of the longitudinal and lateral dimensions is usually done for the catchment surface using topography (Murphy *et al.*, 2008) and has received attention in recent years, including temporal patterns of expansion-contraction of streams and wet areas (Ågren *et al.*, 2015). However, variations in vertical connectivity to the stream down the riparian profile have been overlooked or assumed trivial. The proposed DSL concept (that was quantified for DOC in paper II) implies that

the mobilization of solutes to streams is limited to only a fraction of the total RZ volume. Therefore, stream chemistry will be determined by the biogeochemical processes occurring in the DSL almost independently on the rest of the RZ, which only contribute to a small fraction of the water and solute fluxes.

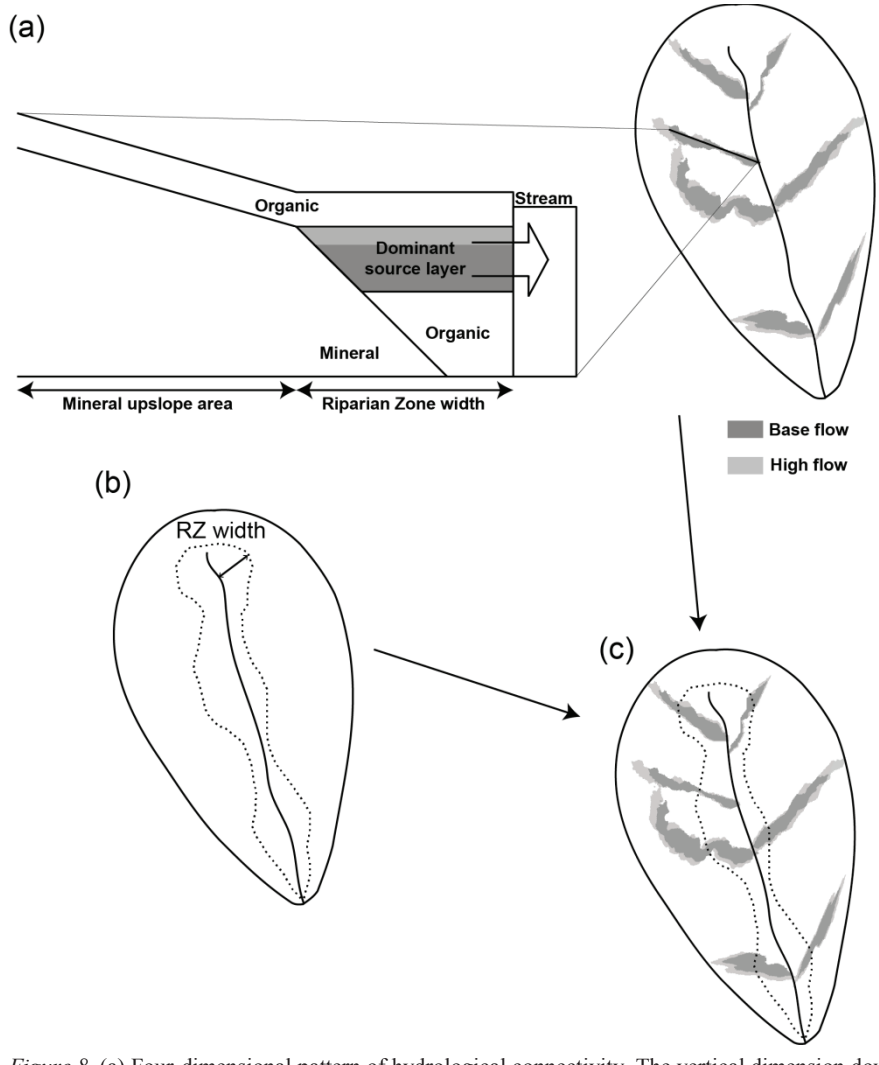

Figure 8. (a) Four-dimensional pattern of hydrological connectivity. The vertical dimension down the riparian profile is characterised by the dominant source layer. Grey areas represent two dimensions: longitudinal along the stream and lateral along the hillslope. The temporal dimension expand, contract, or move the three spatial dimensions. (b) Conceptualization of the heterogeneous spatial distribution of riparian zone (RZ) widths along the stream. (c) Overlapping between hydrologically connected areas and RZ widths. Figure adapted from paper IV.

In addition to being the main source of OM to streams, RZs can either retain or transform the elements and compounds from upslope inputs, in-situ atmospheric deposition, or in-situ weathering on their way to the stream (Figure 9). Retention of elements in the RZ is determined by interactions with OM. For example, -OH and –COOH groups of the OM interchange their protons with cations in the solution causing retention of elements. In paper I, it was shown that the RZ retain BC to a low extent, appearing to act as a conduit for these elements. However, heavier metal cations have a greater affinity to bind with OM. Forest RZs have been shown to retain Al (Mulder *et al.*, 1991; Pellerin *et al.*, 2002), Fe (Knorr, 2013; Riedel *et al.*, 2013), Hg (Lee *et al.*, 2000), Pb (Klaminder *et al.*, 2006), and other organophilic metals and trace elements (Neubauer *et al.*, 2013; Köhler *et al.*, 2014; Lidman *et al.*, 2014). Persistent organic pollutants (POPs) such as polychlorinated biphenyls (PCBs) and certain pesticides have high affinity to bind to OM (via hydrophobic interactions), and are also highly retained in RZs (Bergknut *et al.*, 2011). The retention function of RZs makes them extraordinary buffers of surface water pollution. However, the high affinity for OM of many of the outlined elements allows for co-transportation when OM is solubilized and mobilized to the streams, potentially leading to surface water contamination.

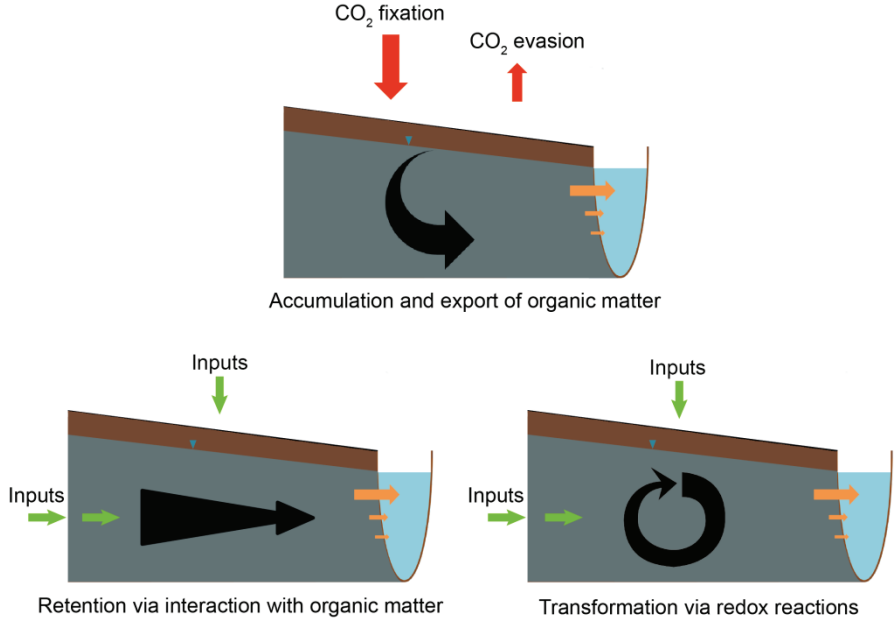

Figure 9. Conceptualization of organic matter accumulation and export and biogeochemical retention and transformation in the riparian zone. Green arrows represent the input of elements via upslope, atmospheric deposition, or in-situ weathering. Orange arrows represent lateral fluxes from to streams, concentrated in a narrow dominant source layer. Figure adapted from paper IV.

The transformation function of RZs occurs via microbial reduction-oxidation processes, where OM is the essential substrate. Although RZs are dominated by hypoxia due to high water levels, transient oxic-hypoxic conditions can occur as a consequence of groundwater table fluctuations, especially in the DSL. Reducing conditions in the RZ may lead to formation of methane (Hope *et al.*, 2001; Sun *et al.*, 2013), removal of nitrate (Simmons *et al.*, 1992; Fölster, 2000; Ranalli & Macalady, 2010), formation of methylmercury (MeHg) (Bishop *et al.*, 1995), or reduction of the oxidation state of metals such as Fe or manganese (Björkvald *et al.*, 2008) that increases its solubility. Episodic oxic conditions in the RZ can lead to the formation of SO_4^{2-} (paper III) or mobile and toxic forms of selenium (Lidman *et al.*, 2011). Therefore, the transformation of compounds in the RZ via redox reaction can buffer potential contaminants (e.g. removal of nitrate), but also create them (e.g. formation of MeHg). Hydrology and time ultimately control mobilization and reaction rates of the retained and transformed elements and compounds in the RZ.

The RZ extent is heterogeneously distributed along the stream (Figure 8b). As it was shown in paper II, this is driven by local hydromorphology that leads to different rates of OM accumulation. Regions with higher OM content appear in wet areas hydrologically connected to streams (Figure 8c). As OM is the key in the RZ biogeochemical functions, the potential for retention or transformation is larger in wider RZs. In other words, the spatially heterogeneous distribution of RZs translates into a heterogeneous intensity of the RZ biogeochemical functions because the longer the RZ width the longer the transit distance of the water in organic-rich layers.

4.4 Implications for the global carbon cycle, future climate, forest management, and riparian upscaling (Papers I-IV)

Given the increasing recognition of the influence of inland waters on the global carbon cycle (Tranvik *et al.*, 2009; Wallin *et al.*, 2013; Hotchkiss *et al.*, 2015), particularly in boreal regions where the carbon stores are globally significant (Gorham, 1991; Yu, 2012), the findings of paper II and paper III are important for global carbon balances. Boreal forest RZs have a long-term potential to transfer DOC to streams from both old and new carbon sources (paper II). Moreover, a synchronous increase in DOC and decrease in SO_4^{2-} concentrations in both RZ and stream was observed (paper III). Declines in SO_4^{2-} deposition is recognized as one of the main drivers of the observed increase in surface water DOC concentrations in Scandinavia, Central Europe, and North America (Evans *et al.*, 2006; de Wit *et al.*, 2007; Monteith *et al.*, 2007). It is proposed that a reduction in SO_4^{2-} in the solution increases humic

charge as acidity and ionic strength decrease, increasing OM solubility (Tipping & Hurley, 1988; Kalbitz *et al.*, 2000; Evans *et al.*, 2012). The present exhaustion of the residual S pool from the peak acidification period, in combination with the long-term potential of RZs to export DOC, is likely to bring DOC concentrations to higher levels affecting surface water quality. Once in the aquatic environment, DOC can be mineralized to CO_2 influencing the global carbon cycle (Battin *et al.*, 2009).

Climate is the other main factor responsible for increasing DOC trends (Hongve *et al.*, 2004; Köhler *et al.*, 2008; Ledesma *et al.*, 2012). However, interactions and covariation between climate and acid deposition makes it difficult to separate their independent effects on DOC. For example, high temperature and low precipitation can lead to depletion of groundwater tables that would favour the oxidation of S compounds in the soil into SO_4^{2-}, which would decrease the solubility of OM (or vice versa). In such a case, the direct cause of a potential decrease (or increase) in DOC would be a chemical effect in the solubility but the compelling force was climate. In paper III, it was shown that SO_4^{2-} controls DOC in a forest catchment such as Krycklan that experienced relatively low rates of anthropogenic acid deposition. This diminishes the relative importance of climate as a driver, which could have an indirect effect on DOC through changing SO_4^{2-} levels. Evaluating drivers of DOC trends without considering SO_4^{2-} could be misleading. Nevertheless, precipitation and temperature do affect primary production and hydrology. Under wetter conditions, forecast for boreal regions (IPCC, 2007), predominant flowpaths and the DSL might shift to upper riparian soil layers with higher DOC concentrations, potentially leading to a higher increase in DOC fluxes relative to the increase in runoff. Higher temperature and precipitation will also tend to increase DOC production (Christ & David, 1996). Combining higher production with shallower groundwater tables in the RZ, which could extend and prolong hypoxic conditions and lower oxidative respiration, the result could be a net increase in NEP. As recently produced carbon is currently enough to support DOC exports (paper II), a future increase in NEP could amplify the transfer of carbon from RZs to streams. However, different studies forecast opposite trends in future NEP for boreal peatland systems such as RZs (Wania *et al.*, 2009; Wu & Roulet, 2014) so potential future changes are uncertain and merit further study.

Hydrological consequences of forest harvesting in boreal regions are similar to those expected by climate change. Both forest harvesting and climate change scenarios resulted in large increases in summer and autumn runoff and higher DOC fluxes in a modelling study in the KCS (Oni *et al.*, 2015). Increased precipitation under future climate and lower evapotranspiration rates after

harvesting would tend to increase groundwater levels. In paper I, it was discussed how an intensification of forestry due to changes in energy policy could shift flowpaths to upper riparian soil layers with a potential to reduce BC fluxes and affect stream acidity. This was supported by a sensitivity analysis of groundwater table variations at the ROK sites. On the other hand, site-specific riparian buffer designs (Kuglerová *et al.*, 2014) should be implemented during forestry operations instead of traditional single riparian buffers because of the spatial RZ heterogeneity. This is especially important in RZs hydrologically connected to the stream in order to preserve riparian function and surface water quality.

The spatial heterogeneity in RZ distribution also implies that single or a few riparian soils might not be representative of the biogeochemistry of the entire catchment. For example, stream and riparian SO_4^{2-} intra-annual dynamics did not entirely coincide (paper III). Specifically, stream SO_4^{2-} concentrations were more dynamic and showed higher peaks than RZ SO_4^{2-} concentrations. The residuals of the regression relating monthly SO_4^{2-} flow-weighted concentrations in stream and riparian site S4 were correlated to the accumulated monthly runoff. Higher positive residuals, i.e. where RZ concentrations under-predicted stream concentrations, were observed during periods with lower accumulated runoff. One interpretation for this phenomenon is that during base flow other riparian areas within the catchment contribute more SO_4^{2-} to stream water than the riparian site S4 (e.g. more organic RZs with higher S pools that are subject to greater oxidization and mobilization during low flow conditions). Concentrations of S were available for riparian site S4 (in the S-transect) and riparian sites R5, R6, R7 (in the ROK) between 2008 and 2009. S concentrations in these four riparian profiles were compared to investigate heterogeneity (Figure 10). S concentrations could be used as a proxy for SO_4 concentrations because 95% of all S mobilized and transported in the catchment is in the form of SO_4^{2-}, as shown in paper III. The comparison revealed that SO_4^{2-} concentration profiles differed among RZs within the C2 catchment. Thus, vertical changes in flowpaths in the entire RZ area that are driven by amount of precipitation and hydrology are important to infer intra-annual stream chemistry dynamics. The heterogeneity within the RZ clearly limits the extent to which it is possible to infer stream chemistry from a single riparian profile over short time scales (days to months). This highlights the limitation of lumped representations of RZs when upscaling to the catchment level, such as when RIM is used as a model. Distributed representations are needed to accurately upscale the integrated riparian signal to the catchment, especially for short-time scales.

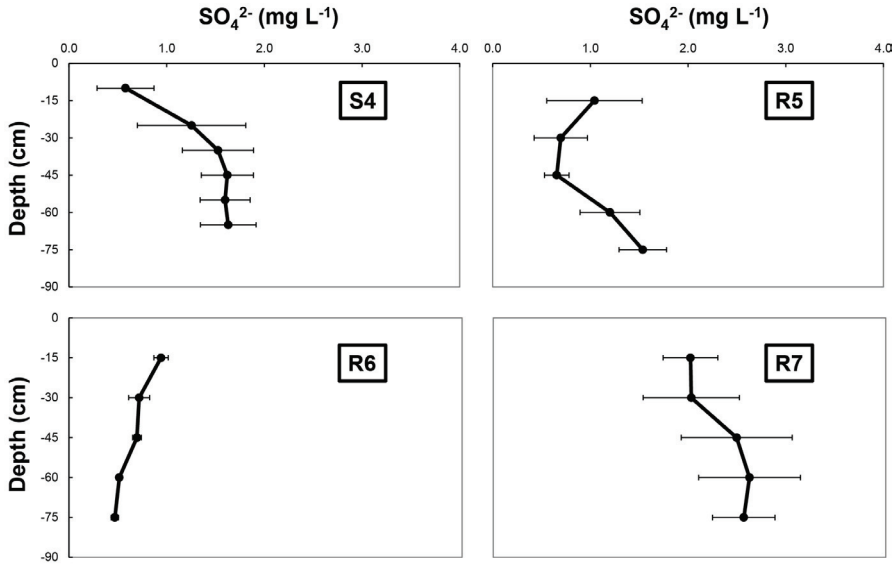

Figure 10. Example of heterogeneous solute profiles within the same catchment. Sulfate (SO_4^{2-}) concentrations (2008-2009) are plotted for riparian sites S4, R5, R6, and R7 within the Västrabäcken catchment C2. Circles represent average concentrations at each layer and horizontal lines are standard deviations. Figure adapted from paper III.

5 Concluding Remarks

This thesis relies on long-term monitoring data, targeted sampling, and field surveys from the Krycklan catchment located in northern Sweden. The extensive network of streams and the unique infrastructure of riparian sites were ideal to investigate terrestrial-aquatic interactions in boreal forests. Overall, this thesis provides new insights into the role of the RZ in catchment biogeochemistry. The main conclusions in relation to the above-mentioned specific objectives are:

- A characteristic upslope mineralogical signal of BC and Si is maintained through the RZ and subsequently exported to the stream waters. The RZ appears to act as a conduit for Ca, Mg, and Na, whereas Si seems to be retained along the riparian matrix.
- There is a potentially long-lasting supply of DOC (in the order of hundreds to a few thousands of years) from RZs to streams. However, despite the large store of carbon in the RZ, the dynamic allocation of new carbon from riparian production seems to control the DOC output.
- RZ processes control stream SO_4^{2-} and subsequently DOC independently of upslope soils. Observed opposite SO_4^{2-} and DOC trends in stream and riparian water suggest that SO_4^{2-} is still an important driver of DOC in boreal catchments.
- A relatively narrow depth range within the RZ has the highest contribution to solute and water fluxes to the stream. This is the dominant source layer 'DSL', an important dimension in hydrological conductivity. RZs are heterogeneously distributed in space as driven by local hydromorphological variations that lead to different rates of OM accumulation. The heterogeneous distribution of RZs in space translates into a heterogeneous magnitude of the

element-specific RZ functions, including retention via interaction with OM and transformation via redox reactions.

- The exhaustion of the residual S pool accumulated during the acidification period, in combination with the long-term potential of RZs to export DOC, is likely to bring DOC concentrations to higher levels affecting surface water quality and the global carbon cycle. Moreover, future predictions of increased precipitation in boreal regions could shift predominant flowpaths to upper riparian soil layers with higher DOC concentrations, potentially leading to a higher increase in DOC fluxes. Both riparian upscaling and successful management needed for sustainable forestry must consider hydrological connectivity, biogeochemical function, and spatial heterogeneity in RZs so as to better understand processes and to preserve water quality in boreal forest catchments.

6 Future Perspectives

Science, as the combination of tools seeking for rational explanations of the behaviour of the Universe, is built upon small pieces of research. These contribute to generate knowledge and serve to further develop new ideas and new research. The contribution that this thesis provides to the behaviour of natural systems, specifically RZs in boreal forests, leaves many unanswered questions and opens new possibilities for future research and practical applications in management.

RZs have been shown to buffer acidification effects via chemical interchange between the riparian soil particles and the solution (Lawrence *et al.*, 1988; Löfgren *et al.*, 2011). This implies that the RZ would be acting as a regulator of BC. The question that arises is how long a change in upslope signal caused by e.g. harvesting would be delayed or attenuated in the stream by the RZ. This could be investigated by comparing lateral fluxes and stores in different, operationally defined pools in the RZ, similar to the approach used in paper II for DOC. Alternatively, scenarios in which upslope fluxes are varied and a geochemical model applied to the RZ, e.g. Visual MINTEQ (Löfgren *et al.*, 2010), PHREEQC (Karlsen *et al.*, 2012), ForSAFE (Wallman et al., 2005), or MAGIC (Cosby *et al.*, 1985), can help estimate when signal changes will be seen in the streams and analyze the magnitude of the RZ buffer effect. BC and SO_4^{2-} were studied separately in this thesis but they should be integrated in future studies as their mobilization is usually coupled as to maintaining the charge balance.

Despite the overwhelming evidence provided by quantitative studies that RZs are the sources of DOC to boreal streams, few studies have compared carbon quality in streams, RZs, and upslope areas (Sanderman *et al.*, 2009). A set of water samples from streams, RZ, and upslope soils could be analysed for absorbance and using fluorescence techniques. Fluorescence measurements can provide reliable information of the source, redox state, and biological reactivity of OM and are rapid, precise, and inexpensive (Fellman *et al.*, 2010).

The mechanisms by which metals such as Al or Fe, are retained in RZs (flocculation-precipitation, oxidation, ion exchange) are not fully understood and should be a focus of further research. These are quantitatively important elements in boreal catchments (Temnerud *et al.*, 2014) that are partially responsible for negative effects in waters, including browning (Köhler *et al.*, 2013).

Future scenarios in which groundwater tables vary as a function of climate or forestry operations could be coupled with a RIM model-type approach to develop storylines about possible future effects on lateral fluxes of different elements, similar to the method used by Oni *et al.* (2015) for DOC. In such a study, the heterogeneity of RZs should be considered.

Another interesting question to answer would be for how long RZs will be using residual S from the acidification period to export SO_4^{2-} and suppress the solubility of DOC, and whether the increasing DOC trends in surface waters will be halted after that. In this context, it would be most useful to integrate all biological processes controlling production, chemical factors (ionic strength, pH, Al concentrations) controlling solubility, climate variables operating in both, and hydrology as engine of exports and controlling short-term variations (Clark *et al.*, 2010). For example, small scale or experimental work with riparian soils could be done to disentangle the importance of plant species and belowground biomass in the production of carbon versus chemical factors in the solubility. Importantly, the degradation/decomposition of OM in riparian soils versus the rest of the catchment should be fundamentally different because carbon cycling in upslopes is biologically controlled by fungal species (Clemmensen *et al.*, 2013) that generally do not tolerate hypoxic riparian peat conditions (Brady & Weil, 1999). Measurements of CO_2 production and release to the atmosphere in riparian and upslope soils would also be interesting in this context. All these studies would need the integration of different disciplines in a holistic approach.

High resolution DEMs based on LiDAR data can be implemented to establish spatiotemporal hydrological connectivity (Ali & Roy, 2010; Ågren *et al.*, 2014). The depth-to-water (DTW) index derived from DEMs can be used to determine soil types (Murphy *et al.*, 2011), although identification of organic soils and thus RZ widths appears to be challenging. In any case, the advances made in remote sensing techniques open a way forward to be able to map both RZ widths and hydrological connectivity and should be implemented in future research.

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Acknowledgements

Thank you for turning to this page. I hope you enjoy reading this section but do not forget that there are many other interesting chapters contained in this book! I will make it excessively long though, so you guys at least make some effort. Okay, now that lazy ones have stopped reading I can freely write about (include grammatical errors) and thank some of the many important persons who, in one way or another, have influenced me and thereby this thesis (or both). I will start with my five (!!) brilliant supervisors.

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